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Relationship of soybean oil quality with completeness of extraction

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RELATIONSHIP OF SOYBEAN OIL QUALITY WITH COMPLETENESS OF EXTRACTION

by

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ABSTRACT

It has been generally assumed that the last portions of oil obtained by extraction become progressively poorer in quality. The purpose of this research was to study the quality of the soybean oil obtained by continuous countercurrent extraction using commercial hexane as solvent. The extractions were carried on to different degrees in the Iowa State University pilot plant extractor by controlling the operating variables, such as the feed rate, the solvent rate, the time of extraction, and the temperature of extraction, and the data on the quality of oil, expressed in terms of iodine value, saponification value, refining loss, refractive index, nonsaponifiable matter, and color, were correlated with the completeness of extraction.

The speed of the conveyor chain was varied from 1.6 to 5.5 inches per minute, the feed rate varied from 3.50 to 7.29 pounds of flaked soybeans per hour, on the dry basis, the solvent rate varied from 2.50 to 8.00 pounds per hour, the extraction time from 19.1 to 65.6 minutes, and the extraction temperature from 133.0 to 155.4°F.

Analytical results showed that, with the residual extractables remaining in the meal varying from 4.24 to 0.68 percent, there was a trend of continuous decrease in the corresponding iodine value and saponification value, but that the variation was small. The refining loss of the oil increased

rapidly below 1.0 percent residual oil in the meal. It is, therefore, not advisable to extract soybeans down to the very low oil level. Perhaps 1.0 percent residual oil is a good criterion for solvent extraction of soybeans.

INTRODUCTION

The soybean has been extensively cultivated and highly valued as a food in China since prehistoric times (48). From China the soybean has spread over a considerable portion of the world. It was first introduced into the United States early in the nineteenth century, and its production has been climbing rapidly since then. The principal soybean producing countries at present are the United States, China, Indonesia, and Japan in the order named. The world production of soybeans in 1959 is given in Table 1 (4).

Table 1. World soybean production in 1959

	Thousand bushels
United States of America	537,895
China	350,000
Indonesia	17,000
Japan	15,708
Others	33,442
World total	954,045

Before 1935 the soybean in the United States was principally grown as a forage crop in the southern and south-eastern states, North Carolina, Virginia, Mississippi, Kentucky, and Alabama. Now the industry is largely centered in the five states comprising the Corn Belt, i.e., Illinois, Iowa, Indiana, Ohio, and Missouri, and the marked increase in the production

of soybeans in the United States has led to the development of numerous industrial uses for both the oil and the meal. The utilization of soybean products in the United States for the crop year 1958-59 is shown by percentages in Table 2 (4).

Table 2. Utilization of soybean products for crop year 1958-59

	%
Soybean oil meal	
Livestock feed	96.0
Industrial	0.1
Export	3.9
Total	100.0
Soybean oil	
Edible	92.2
Industrial	7.8
Total	100.0

The chief outlets for soybean oil are in the production of shortenings and margarine. The trends of soybean oil consumed in food use from 1931 to 1955 are summarized in Table 3 (6).

The soybean or soybean products are used industrially in such products as coated papers, leather dressings, fire-fighting foams, glues, plywood adhesives, insecticides, laminatings, lecithins, oil cloths, coated fabrics, paints and varnishes, paper sizings, resins, soaps, and fatty acids.

Prices received by farmers for the soybean averaged at $2.00 per bushel of 60 pounds, or approximately 3.3 cents per pound in the crop year 1958-59 (4). The crude soybean oil was

Table 3. Soybean oil consumed in food use

Period average	Margarine			Shortening			Other edible		
	Total fats & oil	Soybean oil		Total fats & oil	Soybean oil		Total fats & oil	Soybean oil	
	million pound	million pound	% of total	million pound	million pound	% of total	million pound	million pound	% of total
1931-35	217	1	0.46	1,183	14	1	667	12	2
1936-40	293	49	17	1,468	151	10	883	76	9
1941-45	424	165	39	1,406	485	34	963	199	21
1946-50	655	251	38	1,493	742	50	1,086	264	24
1951-55	1,025	652	64	1,731	867	50	1,431	448	31
1955	1,075	746	69	1,988	930	47	1,661	584	35

sold for 9.5 cents per pound average at Chicago and the meal, bagged, in carlots, at Chicago, for $65.50 per ton average, or approximately 3.27 cents per pound in the crop year 1958-59 (4).

Three processes are employed in removing soybean oil from soybeans. They are (a) the solvent extraction process, whereby flaked soybeans are leached or extracted with a solvent such as hexane, (b) the screw press process, which utilizes a worm shaft continuously rotating within a pressing cylinder or cage to express the oil from soybeans after they have been crushed and properly dried, and (c) the hydraulic process, whereby an intermittent pressing operation is carried out at elevated temperature in a hydraulic press after the beans have been rolled into flakes and cooked. Solvent extraction recovers 95 to 98 percent of the oil in the soybean, while mechanical expression removes only about 75 to 80 percent of the oil.

The greater yield of oil obtained with solvent extraction has been a sufficient incentive to cause the erection of a large number of solvent extraction mills in very recent years. In the crop year 1945-46, the percentages of the total quantity of soybean crushed in the United States by hydraulic press, screw press, and solvent extraction, respectively, were 7.6, 64.2, and 28.2, with average oil yields per bushel being respectively for the three processes, 8.46, 8.86, and 10.67

pounds. In 1949-50, the corresponding percentages had changed to 2.9, 41.2, and 55.9, i.e., solvents were used to process more soybeans than the screw press method, for the first time. In 1951-52, almost three times more soybeans were processed by solvent equipment than by the screw presses -- 74 percent of the total crush as compared to 25 percent. The remainder were crushed by hydraulic presses (63). In 1957-58, 93 percent of the soybean was processed by the solvent method of extraction (54).

It is now considered that the efficient commercial solvent extraction for soybeans must reduce the oil content of the dry solid residue to less than 1.0 percent. However, Bull and Hopper (17) studied the composition of crude lipids obtained from soybeans by successive extractions with Skellysolve F[a] and with Skellysolve B[b] and found that the last portions of the oil were high in phosphatides and low in iodine number. The fractions of oil obtained by extraction with Skellysolve F had iodine numbers from 132.4 to 114.9 and phosphatides from 0.53 to 23.95 percent, while the Skellysolve B extractions gave iodine numbers from 129.7 to 119.6 and

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[a]Skellysolve F is essentially a pentanes-hexanes fraction. Its physical properties as given by the Skelly Oil Company are as follows: boiling range, 95-130°F, specific gravity, 0.638.

[b]Skellysolve B is essentially a normal hexane fraction. Its physical properties as given by the manufacturer are: boiling range, 146-157°F, specific gravity, 0.686.

phosphatides from 1.29 to 18.62 percent. Ayers and Scott (8) had studied quality of soybean oil in multiple stage extraction and found that certain constituents of the oil were removed "in quantity" only during the final stages of extraction. Karnofsky (37) reported that the quality of the crude oil became progressively poorer in the final stages of extraction and that the last portions of oil were extremely high in refining loss. Therefore, it does not at all appear certain that there is a clear advantage in extracting soybeans down to the very low oil level. On the contrary, it is entirely possible that the addition of such undesirable material to good oil could more than counterbalance the increased oil yield and might actually reduce the amount of material recoverable as refined oil.

The data of Bull and Hopper (17) were obtained by multiple stage extractions but thus far correlations of this type of data with continuous countercurrent extractions have not been found in the literature. It is the purpose of this project to study the quality of the soybean oil obtained by continuous countercurrent extractions and to correlate the variation in the quality with the completeness of extraction, or, in other words, with the residual extractables in the extracted meal.

REVIEW OF LITERATURE

Composition and Characteristics of Soybeans and Soybean Oil

The seeds of the soybean plant, like all other seeds, are extremely complex in chemical construction. Variations in composition are considerable due to varietal differences, climatic and soil conditions under which they are grown, as well as other environmental factors.

According to the investigations of Cartter and Hopper (18) the oil content of the soybean seed was most specifically a varietal characteristic, and the iodine number of the oil was about equally influenced by variety and climate. Temperature levels significantly influenced the calcium content of the seed produced by a given variety. Invariably high calcium content resulted when the soybeans were grown at high temperatures. Total ash, phosphorus, and potassium content of the seed appeared to be influenced more by soil type and fertility than by variety or variation in climate.

Collins and Cartter (21) observed marked difference in oil content of soybeans as a result of difference in position of pod on the plant, position of pod on the raceme, and position of the seed in the pod.

The results of Bailey, Capen, and LeClerc (10) as indicated in Tables 4 and 5 may serve as a good reference of the composition of soybeans. Similar results were also reported by Gabby (28) and Morse and Cartter (49).

Table 4. Chemical composition of soybeans

	Minimum %	Maximum %	Average %
Moisture	5.02	9.42	8.0
Ash	3.30	6.35	4.6
Fat	13.50	24.20	18.0
Fiber	2.84	6.27	3.5
Protein	29.60	50.30	40.0
Pentosan	3.77	5.45	4.4
Sugars	5.65	9.46	7.0
Starch-like substances by diastase	4.65	8.97	5.6
P_2O_5	1.50	2.18	1.7
K_2O	2.01	2.64	2.3
CaO	0.49	0.63	0.5
MgO	0.46	0.55	0.5

Table 5. Composition of the component parts of soybeans

	Proportion of the seed %	Moisture %	Protein %	Carbo-hydrates %	Fat %	Ash %
Cotyledons	90	10.57	41.33	14.60	20.75	4.38
Germ	2	12.01	36.93	17.32	10.45	4.08
Seed coat	8	12.53	7.00	21.02	0.60	3.83

The physical and chemical characteristics of crude soybean oils show considerable variations resulting from combinations of the inherent properties of the seed and the methods of extracting the oil. The crude oil consists principally of the glycerides of saturated and unsaturated fatty acids, admixed with a number of minor constituents, such as the phosphatides, sterols, long chain hydrocarbons, alcohols and ketones, free fatty acids, pigments, vitamins, antioxidants, and gummy or mucilaginous substances.

Alderks (2) examined thirteen specimens of soybean oil from experimental strains of beans grown in Indiana, Illinois, Iowa, and Ohio. The extremes of iodine values were 128.7-136.6 and of component acids, saturated 16-19, oleic 11-12, linolenic 6-8.5 percent. Collins and Howell (22) studied soybean oil from different locations and varieties and found that location composites varied from 5.9 to 8.3 percent in linolenic acid and from 45.3 to 50.4 in linoleic, and that variety composites varied from 5.4 to 8.0 percent in linolenic and from 43.9 to 51.6 percent in linoleic. The effect of external factors on the chemical composition of the component glycerides of the soybean oil was also investigated by Blackmore (13) and Simmons and Quackenbush (62). Krober and Collins (40) observed that the percentage of extractable material obtained was highly dependent upon the atmospheric conditions under which the sample was analyzed.

A complete analysis of the component acids of soybean oil has been given by Hilditch and Jasperson (31) and Alderke (1). More recent information is from the Spectroscopy Committee (67) of the American Oil Chemists' Society. These data are reproduced in Table 6.

Table 6. Comparison of analysis of soybean oil by different methods

	Number of laboratories making the determinations	Avg. values found Oil No. 3	Oil No. 4
Iodine value	4	135.8	135.8
Thiocyanogen value	2	84.8	85.0
Saturated acid, by Bertram method	2	15.2	14.9
Saturated acid, by Twitchell method	1	12.6	12.0
Saturated acid, average of 3 methods		14.2	14.0
Composition from thiocyanogen analysis			
Oleic acid		25.6	26.1
Linoleic acid		49.6	49.2
Linolenic acid		10.6	10.7
Composition by spectrophotometric analysis			
Saturated acids		14.0	14.0
Oleic acid		22.9	23.0
Dienoic		55.2	55.0
Trienoic		7.9	8.0

Notwithstanding that individual oils derived from specific varieties of seed may show wide variation in physical properties and chemical compositions, Markley and Goss (45)

pointed out that commercial soybean oils are much more uniform owing to the mixing of different lots of seeds, and of different batches of oil during processing. Furthermore, the numerous refining operations tend to eliminate much of the secondary materials, especially gums, phosphatides, free fatty acids, unsaponifiable matters, and pigments. The characteristics of soybean oil in Table 7 are taken from the textbook by Eckey and Miller (26).

Theory and Mechanism of Extraction

Boucher et al (14) conducted extraction experiments with chlorinated hydrocarbons on porous clay plates saturated with soybean oil and concluded that the extraction process was one of pure molecular diffusion, the diffusion coefficients being substantially constant for any one temperature and system, independent of liquid concentration, despite the large difference in the solute and solvent viscosities. The authors were able to solve the second order differential equation of Fick's law of diffusion through liquids, derived by analogy to the laws of heat transfer, and found that their experimental data checked with the theoretical values as calculated from the Fick's law equation.

King et al (39) in extraction of soybean flakes with trichloroethylene found that simple diffusion theory failed to fit the soybean data. They suggested that the structure of

Table 7. Soybean oil characteristics

	Usual range	A.O.C.S.	British standards	Typical specimen
Acid value	0.3-3	--	3 max.	0.9
Saponification value	189-195	189-195	190 min.	193.5
Iodine value	117-141[a]	120-141	129-143	131.6
Thiocyanogen value	77-85	79	--	81.3
Diene number	--	--	--	0.7
Hydroxyl value	4-8	--	--	5.8
R-M value	0.2-0.7	--	--	--
Polenske value	0.2-1	--	--	--
Unsaponifiable, %	0.5-1.6	1.5 max.	1.2 max.	0.84
Volatile matter, %	--	--	0.2 max.	--
Refractive index, 25°C	1.471-1.475	1.470-1.476	1.473-1.477[b]	1.4727
Specific gravity, 25/25°C	0.916-0.922	0.917-921	0.924-0.928[c]	0.9195
Titer, °C	22-27	--	--	--
Color, 1" cell	--	--	60Y, 6R max.	35Y, 4R

[a]Commercial oils mostly within the range 127-138.

[b]At 20°C.

[c]At 15.5/15.5°C.

the soybean flakes and the distribution of the extractable material in the flakes might be responsible for the discrepancy. Osburn and Katz (51) pointed out that structure of the solid was a variable in the application of diffusion theory to extraction and recommended that extraction of soybean flakes could be visualized as the simultaneous operation of two different diffusion processes with different diffusion coefficients.

Fan and co-workers (27) reported a study of diffusion phenomena occurring during solvent extraction of peanut oil from specially prepared sections of peanut kernels. They observed that the diffusion coefficient varied with solvent and with the moisture content of the oil seeds but was essentially independent of the thickness of the peanut sections extracted.

Ruth (59) developed an equation for calculating the time of extraction and a method for solving extraction problems semigraphically by applying solute and solution balances progressively from unit to unit. Smith (66) presented an empirical method of calculating the rate constants from residual oil content and extraction time data.

As a result of extensive experimental work, Karnofsky (37) found that the mechanism of extraction appeared to be a combination of diffusion, dialysis, and the solution of slowly soluble extractable material. Coats and Karnofsky (19) observed that the rate of solution of the oil was mainly a matter of soaking time. Soaking in any concentration of miscella

below 20% for half the total extraction time required to reduce the undissolved oil to 1% was just as effective as extraction for the entire time with fresh solvent.

The study of the extraction of oil seeds is complicated by the fact that the total extractable material is variable in quantity and composition, depending on the solvent and other factors. Coats (19) suggested that the difficulty of extracting the last portions of oil from oil seeds might be related to the chemical composition of the oil. Bull and Hopper (17) in the study of extraction of lipids from soybeans reported that there was first a rapid extraction of the triglycerides and following this a slower removal of the portions which were less accessible, that there were removed compounds which were less soluble in the solvent and which were only completely removed after more extensive extraction, and that the extraction of phosphorus compounds started more slowly than that of any other constituent.

The effects of particle size, temperature of extraction, and moisture content of sample on rate of extraction have been studied by Coats and Wingard (20), Karnofsky (37), and Wingard and Phillips (69). Arnold and Patel (7) reported that over the range of usual practical plant operating conditions the effect of moisture on the rate of extraction was small.

It has long been recognized that the extraction of oil from raw cottonseed meats, copra, peanuts, and other high oil-bearing seeds and nuts is more rapid if these commodities are

first prepressed and flaked. The investigations of Dunning and Terstage (25) on the prepressing of soybean prior to solvent extraction, however, showed that the prepressed, conditioned, and flaked soybean cakes even at less than 10% oil content did not show a higher rate of extraction over standard soybean flakes.

Experiments by Othmer and Agarwal (52) indicated that diffusion was relatively unimportant in oil extraction, and that rate of extraction could be correlated as a function of flake thickness and of percentage oil remaining in the flakes.

Othmer an Jaatinen (53) found that the extraction action of different solvents depended on relative physical properties. Rates of extraction were increased by low viscosities, high densities, and high surface tensions. They also suggested the mechanism of extraction as follows: Initial contact of solvent dissolves oil from the flake surface and the outer layers of broken cells. The solvent then penetrates into the voids and capillaries to dissolve more oil. Concentration differences occur in the maze of capillaries; and capillary flow moves the oil nearer the bulk miscella, where further solution occurs. As oil concentration in the flake decreases, the concentration gradient decreases, and oil concentration increases in the extracting miscella. The potential for flow, therefore, also decreases; and the rate decreases rapidly down to the equilibrium oil condition, where further extraction ceases.

It may be well concluded that the rate of extraction is influenced by a number of factors. These include the diffusion coefficients of the solvent and the oil, the size and shape of the flakes, the internal structure of the seed particles, and, at low seed oil levels, the rate at which the solvent dissolves non-glyceride substances which are oil soluble but which dissolve less readily than the glyceride portion of the oil.

Commercial Processing Equipment and Operating Conditions

Extractors are divided roughly into the total immersion type, which are usually strictly countercurrent, and the percolation type, which usually have an initial concurrent and filtering section followed by a countercurrent section. Examples of the immersion types in the United States are the Anderson and the Allis-Chalmers extractors. Another example of commercial equipment, embodying the principles developed at the Chemical Engineering Department of Iowa State University, has been manufactured by the Crown Iron Works Co., Minneapolis, Minnesota. The percolation type of extractors in commercial use are the French basket-type extractor, the Blaw-Knox Rotocel extractor, and the filtration extractor. A description of the equipment in detail can be found in Bailey's (9) textbook or elsewhere in the literature.

The step by step operations of processing soybeans by commercial solvent extraction plants were given by Tennent

(68) as follows:

Cracking -- There are two-pair-high and three-pair-high cracking rolls. These are corrugated in spiral of about 2 to 3 inches in the 42-inch rolls. The bean should be cracked into pieces small enough to make a flake about the size of a dime after flaking.

Flaking -- The flaking rolls are either one pair or two pairs in one frame. The flakes will extract or give up the oil better if they are from 0.006 to 0.008 of an inch in thickness. Flaking temperatures range from 135 to 138°F.

Extraction -- The flakes are first introduced to what is called half-miscella.[a] This is hexane with less than 15 to 18% oil content. The extraction temperature is around 135°F.

Evaporator -- The full-miscella is pumped to the evaporator, where at least 90 to 95% of the hexane is evaporated off. The temperatures in the evaporator range from 210 to 230°F.

Vacuum stripper -- The final traces of hexane are stripped from the oil in a vacuum stripper at 220 to 240°F under 22 to 26 inches of vacuum.

Detailed data for designs, specifications, and operating requirements of solvent extraction mills, and data for investment payout and manufacturing return have been made available by Brewster and Mitchell (15) and Becker and McCubbin (12).

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[a]In some extractors hexane instead of half-miscella contacts the flakes first.

PILOT PLANT EXTRACTION INVESTIGATION

Equipment

Flaking equipment

Two different sets of equipment were used in the preparation of flakes.

In one set of equipment manufactured by the Allis-Chalmers Company the soybeans were fed into a wooden bin from which they were conveyed through a tempering section by a screw conveyor. The tempered soybeans were then cracked between a pair of corrugated rolls 9-1/2 inches in diameter and 14-1/2 inches in length. The cracked beans were flaked between another pair of rolls having same dimensions as the cracking rolls but with flat surface.

In other equipment the soybeans were first cracked by an attrition mill. Tempering was done prior to flaking by heating the cracked beans in a steam jacketed tube. The cracked and tempered beans were then flaked on a pair of rolls 17-1/2 inches in diameter with 1-5/8 inch faces.

In some of the preliminary runs, the soybeans were flaked on the smaller machine, while in the latter stage the equipment manufactured by the Allis-Chalmers Company was used exclusively.

Pilot plant extractor

The Iowa State University pilot plant extractor used in this work was developed by the Chemical Engineering Department

at Iowa State University, as a result of over 20 years of research. It was featured with a closed loop conveyor chain of the Redler type. The chain was 25 feet in length and consisted of modified circular flights, 2 inches in diameter, attached to standard No. 35 roller chain. The loop casing enclosing the chain conveyor was made of standard 2-inch pipe. Solvent and flakes were introduced countercurrently. The lower part of the loop, where extraction was performed, was heated by a steam coil. The temperature was measured by ten equally spaced copper-constantan thermocouples. The upper part of the loop was surrounded by a steam jacket of standard 4-inch pipe and served as the first desolventizer or drier. Extracted meal was discharged from this first drier into the second drier by a stirrer. Discharge of meal from the second to the third drier was by gravity through a vertical chute. All drier sections were insulated with standard pipe coverings. The second and third driers consisted of 2-1/2 inch pipe surrounded by 4-1/2 inch steam jackets equipped with spiral ribbon conveyors. Solvent removed from the meal was condensed in a water cooled condenser and collected. The dried meal was discharged at the left end of the last drier.

The main drive section was a 3/4 horsepower motor, which was connected through a speed reducer and a series of chains and sprockets to the conveyor chain in the extraction loop and to the spiral ribbon conveyors in the drier section.

The speed of the conveyor chain could be varied by changing the combination of sprockets so that different feed rate or extraction time could be used.

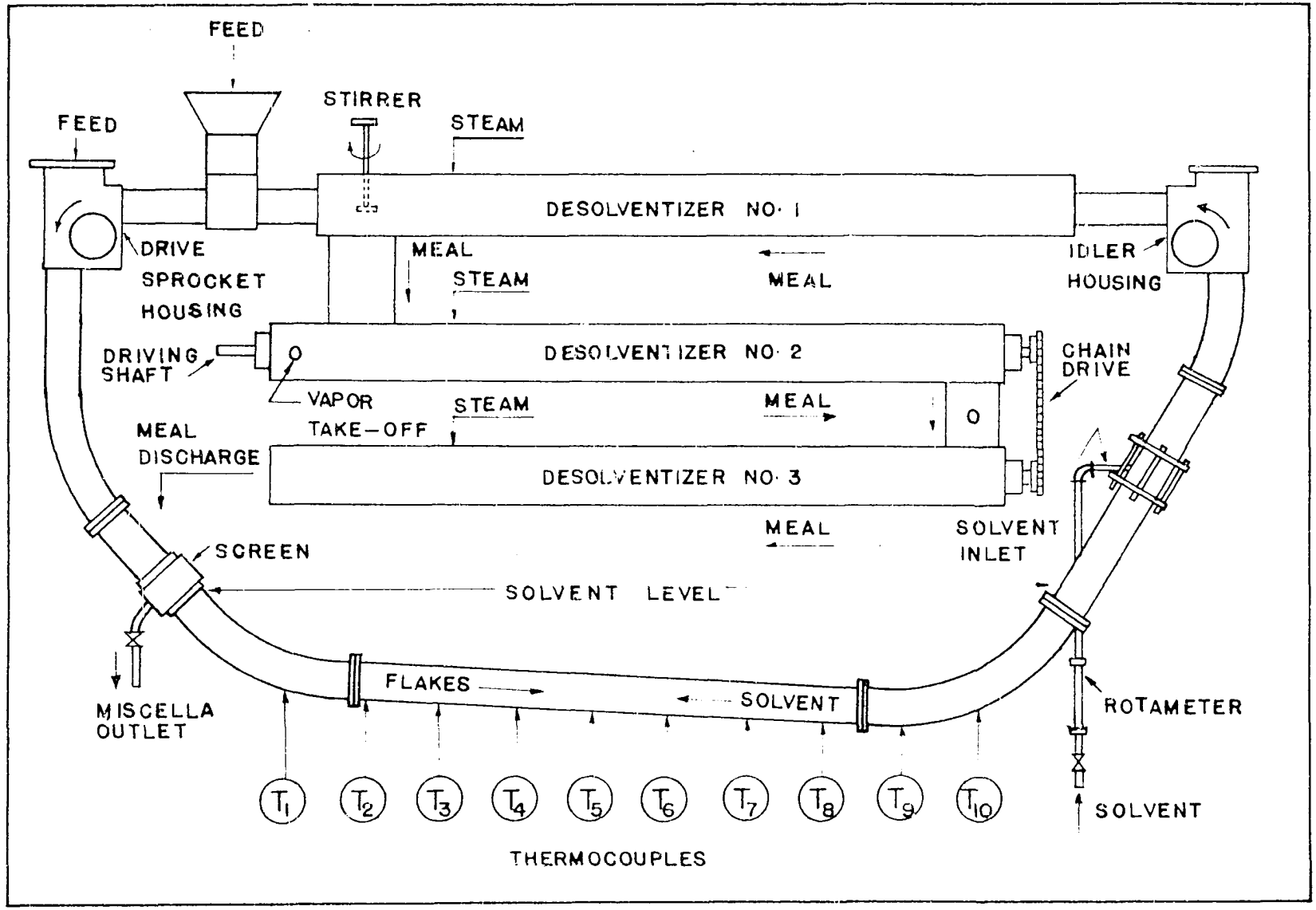
The solvent flow was regulated by a 1/4 inch valve and the rate could be read from a rotameter.

A flow diagram of the pilot plant extractor is given in Figure 1.

Solvent recovery unit

In the beginning, a pilot plant solvent recovery unit was used to separate the solvent from the oil. The unit consisted of a filter, a rising film evaporator, a falling film evaporator, and a stripping column. The miscella from the extractor was first filtered through a Sparkler horizontal plate filter to remove the fines and then fed to the rising film evaporator, which consisted of two long tubes made from standard 1/2-inch pipes with steam jackets. The partly concentrated miscella was discharged into a flash chamber to separate the vapor and the liquid. The vapor was condensed and recovered. The liquid further passed through a falling film evaporator and a stripping column packed with Berl saddles. The stripping column was made from standard 4-inch pipe jacketed with standard 6-inch pipe. Direct steam entered at the bottom of the column to strip the miscella of the last portions of solvent. Heat could also be supplied to the column by indirect steam in the steam jacket.

Figure 1. Flow diagram of the pilot plant extractor


FEED
FEED
STIRRER
STEAM
DESOLVENTIZER NO. 1
DRIVE
SPROCKET
HOUSING
MEAL
STEAM
MEAL
IDLER
HOUSING
DRIVING
SHAFT
DESOLVENTIZER NO. 2
CHAIN
DRIVE
VAPOR
TAKE-OFF
STEAM
MEAL
MEAL
DISCHARGE
DESOLVENTIZER NO. 3
MEAL
SOLVENT
INLET
SCREEN
SOLVENT LEVEL
FLAKES
SOLVENT
MISCELLA
OUTLET
ROTAMETER
SOLVENT
T1
T2
T3
T4
T5
T6
T7
T8
T9
T10
THERMOCOUPLES

A mixture of solvent vapor and water vapor from the top of the column passed first through a trap to separate any entrained oil drops and then through a condenser. The condensed mixture of solvent and water went into an enclosed tank where water settled to the bottom and was drawn off.

The oil flowing out the bottom of the column usually contained small amounts of water in emulsion which was separated later.

The pilot plant solvent recovery unit gave an oil of dark color, which could be improved by refining but which did not seem satisfactory for our subsequent purposes of quality evaluation. Thus, solvent removal was later done on a bench scale with laboratory glasswares. In this case, the miscella was first filtered through a glass funnel to remove the fines. The filtered miscella was transferred into a distillating flask and a large portion of the solvent was distilled off by heating on a water bath under reduced pressure. To remove the last traces of the solvent the oil was finally heated in a vacuum oven manufactured by the Geo. T. Walker and Company.

Analytical Procedures

Moisture content of flakes or meal

The American Oil Chemists' Society method (3) was used to determine the moisture content of the flakes or the meal. A sample of about 10 grams was dried in the oven at $130^{\circ} \pm 3^{\circ}C$

for three hours and the loss in weight was reported as percentage of moisture content.

Oil content of seed or meal

Oil content of the material studied was determined by extraction with normal hexane in a Soxhlet extractor. About 5 grams of the flaked soybeans were placed in the extraction thimble for the determination of oil content in seed, while a ground sample of about 10 grams was used for the determination of the residual extractables in the meal. In each case, the sample was extracted for three hours by hexane at its boiling point, withdrawn from the extraction thimble, reground, and extracted again for another hour. At the end of the extraction, the solution of oil and solvent was filtered into a clean tared flask. After most of the solvent was distilled off on a water bath, the flask and its contents were put in a vacuum oven to remove the last traces of solvent. The oil content was calculated on a moisture-free basis.

Miscella concentration

Miscella concentrations are important data for process control. If the extraction temperature and the miscella concentration remain fairly constant, it can be assumed that a steady state of operation has been reached. The miscella concentrations can be determined either by distilling off all the solvent or, preferably, by measuring the specific gravity, which affords a basis for a rapid determination and which is

also fairly accurate. A specific gravity-composition curve at a convenient temperature was first prepared from which the composition of the miscella could be read when the specific gravity was known. Density-composition-temperature data for binary mixtures of soybean oil and hexane can be calculated from the general formula as suggested by Skau et al (65). The following data in Table 8 were, however, obtained by mixing known amounts of soybean oil and hexane in a tightly stoppered bottle and determining the specific gravities of the respective mixtures at 25°C by weighing in a specific gravity bottle. A plot of specific gravity against percent oil in miscella is given in Figure 2.

Table 8. Specific gravities of hexane-soybean oil miscella at 25°C

Soybean oil gram	n-Hexane gram	Oil %	Specific gravity of miscella
0.0000	--	0.00	0.6632
5.4732	29.2148	15.69	0.6969
9.1416	25.6639	26.26	0.7179
13.0730	22.2385	37.02	0.7476
22.7106	16.1918	58.38	0.7977
--	0.0000	100.00	0.9194

Refining loss

Refining loss is a quantitative criterion of crude oil value. It represents a direct monetary loss to the refiner.

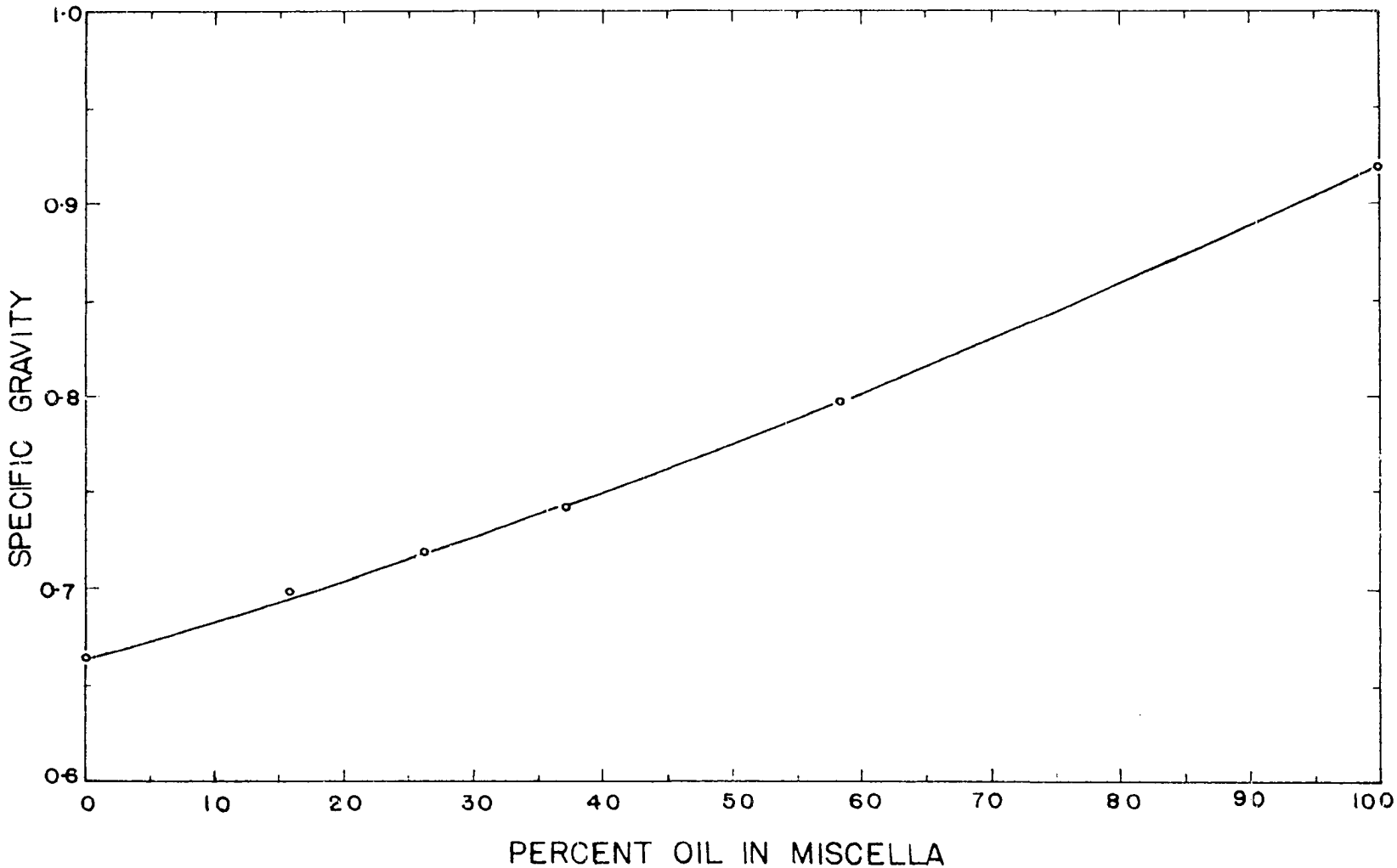


Figure 2. Specific gravity-composition curve of n-hexane-soybean oil miscella at 25°C

The American Oil Chemists' Society (3) has official refining test methods for soybean oils. However, the analysis requires a comparatively large sample of oil. For our pilot plant extraction we prefer to use methods of analysis which can be performed on relatively small samples. Therefore, the chromatographic method (42) and a modified cup method have been studied.

In the chromatographic method a sample of 2 to 3 grams of oil was taken. The oil was first dissolved in 25 ml. diethyl ether and the resulting oil-ether solution was transferred to an adsorption column of activated alumina. The extract from the column was collected. After the solvent was evaporated on a steam bath, the oil was dried at 120°C in an oven. The loss in weight was expressed as percentage refining loss.

The chromatographic method was an easy and rapid method to determine the refining loss of an oil. Reproducible results could be obtained with considerable care. The results, however, were usually much lower than that of the official method. Sipos (64) has been able to correlate chromatographic loss determinations with A.O.C.S. Cup Refining determinations by the ratio of cup loss to chromatographic loss. However, the correlation curves were entirely empirical and lacked generality, as the author himself pointed out that oils from soybeans of different crop years might result in different correlation curves. Thus the chromatographic method was dropped.

In the study of a modified cup method we found that refining losses could be determined with a 50-gram oil sample, i.e., only one tenth of the weight as specified in the official method, without sacrificing the accuracy of the results, if a modified cup of 1-1/4 inches diameter by 4 inches height was used in place of the official 4 inches by 4 inches cup. The design of the modified cup was such as to make the cross-sectional area of the cup per unit weight of the sample approximately the same as that of the official method. In the modified cup method the same procedure of the official method was followed. The only differences were the cup and the weight of the sample.

Besides giving the same results as the official method, the modified cup method had another advantage over the chromatographic method, i.e., by the former method we were able to get substantial amounts of refined oil, which could be used for subsequent analysis. Therefore, the modified cup method was used exclusively in this experiment in determining the refining losses.

Iodine value

The iodine value is a measure of the unsaturation of the oil and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample. The most commonly used method is the Wijs method.

To a sample of about 0.25 gram soybean oil is added 20 ml.

of carbon tetrachloride and 25 ml. of the Wijs solution, the active component of which is iodine monochloride in glacial acetic acid. The contents are kept at room temperature in a dark place for about 30 minutes to react. Potassium iodide solution is then added and the sample titrated with sodium thiosulfate solution using starch indicator. The procedure in detail can be found in Official and Tentative Methods of the American Oil Chemists' Society (3).

Saponification value

The saponification value is a measure of the average molecular weight. The American Oil Chemists' Society official method (3) was followed. A carefully weighed oil sample of about 5 grams is saponified with alcoholic potassium hydroxide. The excess potassium hydroxide is titrated with standard acid. The saponification value is expressed as the number of milligrams of potassium hydroxide required to saponify 1 gram of the oil.

Unsaponifiable matter

Unsaponifiable matter includes those substances frequently found dissolved in fats and oils which cannot be saponified by the caustic alkalis but are soluble in the ordinary fat solvents. Included are the higher aliphatic alcohols, sterols, pigments, and hydrocarbons. The American Oil Chemists' Society official method of analysis (3) was followed.

About 5 grams of the oil is saponified with potassium

hydroxide and then extracted with petroleum ether. The unsaponifiable matter and the fatty acids are soluble in petroleum ether. After evaporating the solvent the residue is dried in a vacuum oven and weighed. After weighing, the residue is taken up in 50 ml. of warm alcohol and titrated with sodium hydroxide. The weight of fatty acids can thus be calculated and be subtracted from the weight of the residue, giving the actual weight of unsaponifiable matter.

Color

The color of the oil can be determined either by the Lovibond method or by the spectrophotometric method (3). However, the latter is to be preferred. In the spectrophotometric method the optical density of the oil sample is measured at four different wavelengths, 460, 550, 620, and 670 millimicrons on a Coleman Junior Spectrophotometer. The color is correlated to the Lovibond scale by the following formula:

Photometric color =

$$1.29\ D_{460} + 69.7\ D_{550} + 41.2\ D_{620} - 56.4 D_{670}$$

Refractive index

The refractive index of the oil has close relation to the average molecular weight and degree of unsaturation. The American Oil Chemists' Society official method of analysis (3) was followed. The refractometer used was manufactured by the Baush and Lomb Company, equipped with a thermostatically controlled water bath and motor-driven pump to circulate water

through the instrument.

Extraction of Soybean Oil

Material

The soybean was a mixture of standard varieties grown on one of the University farms. It had been air dried in our laboratory and had a moisture content of 5.56%. The oil content, or total extractables using hexane as a solvent, was 20.59%, on moisture-free basis.

The solvent was the Phillips 66 high purity normal hexane from the Phillips Petroleum Company.[a]

Preparation of flakes

Yates (70) concluded that the optimum conditions for flaking soybeans were as follows: (a) a moisture content in the bean of 10 to 12 percent, (b) tempering prior to flaking, and (c) cracking the beans before flaking.

According to Boucher et al (14) the rate of extraction varied inversely with the square of the thickness of the particles being extracted. Othmer and Agarwal (52) studied the extraction of soybeans and found that the rate of extraction decreased approximately as the flake thickness raised to the fourth power.

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[a]The physical properties of Phillips 66 high purity normal hexane as given by the manufacturer are as follows: boiling point range, 151°-156°F, specific gravity of liquid at 60/60°F, 0.683.

Therefore, thin flakes are desirable for extraction. However, the flakes must have enough mechanical strength so that excessive breakage into fines will not occur.

Based on the above knowledge, the moisture content of the soybeans was first determined and calculated amount of water was then added to adjust the moisture content to about 10%. The actual moisture content was determined later. The beans, after thorough mixing with the water added, were kept in tightly covered drums and allowed to stand overnight to ensure thorough penetration of water. The beans were then cracked into 6 to 8 pieces, tempered, and flaked.

It was found that flakes tended to deteriorate on storage. The oil obtained from flakes that had been kept for some time usually had higher free fatty acid than the oil from freshly prepared flakes. Thus, the soybeans used for extraction were flaked on several batches and naturally the moisture contents of the flakes were different, because it was difficult to adjust the moisture content exactly to the desired value.

The effect of moisture on the quantitative extraction of lipids from soybeans was studied by Bull (16), who found that the amount of oil extracted increased slightly with moisture contents between 11.4 and 23.4%. Measamer (47) investigated the extraction of soybean flakes with trichloroethylene and found very little difference in the extraction rate with

moisture contents between 0-10%. Arnold and Patel (7) reported that over the range of usual practical plant operating conditions the effect of moisture on the rate of solvent extraction of soybeans and cottonseed meats was small. Therefore, it seemed to be justified in our experiments to use flakes with moisture contents varying in the range of 9.29 to 14.20%. In all cases the average flake thickness was 0.011 inch.

Extraction

The operating variables which can be controlled on the Iowa State University extractor are the extraction time, the extraction temperature, the solvent rate, and the feed rate.

The Iowa State University pilot plant extractor was fitted with a set of sprockets and chains which could be used to vary the speed of the conveyor chain and hence the extraction time. Preliminary runs on the extractor indicated that for soybean flakes an extraction time of 50 minutes or more was needed to reduce the residual oil to about one percent. Since this project was to study the quality of the oil obtained at different degrees of extraction, it was necessary to design the experiments so that in some cases the residual oil content of the meal would be less than one percent while in other cases the residual oil content would be considerably above one percent. Thus, the extraction time was varied over a range from 19.1 to 65.6 minutes.

It is natural to expect that high temperatures are desirable to extraction. P'Pool (57) studied the effect of temperature on extraction and concluded that the residual oil varied inversely as the extraction temperature. Wingard and Phillips (69) and Juhl (36) also found that higher temperatures increased the rate of extraction. If hexane is used as the solvent it appears that the optimum temperatures for extraction are somewhere near its boiling point, i.e., from 151 to 156°F. In some of our experiments we did not intend to extract as much of the oil as possible, and therefore lower temperatures were used.

In solvent extraction of oil the solvent must eventually be recovered from the oil. It is evident that the ratio of solvent to oil must be kept at a minimum so that charges for steam and water for solvent recovery can be as low as possible. In the best continuous countercurrent extraction plants the solvent-feed ratio may be as low as 1 to 1 by weight. In this project the solvent-feed ratio was varied from 0.36 to 2.28.

In an actual run of the pilot plant extractor, the steam was first turned on in the drier section and the extractor loop to warm up the apparatus. Then the extractor motor was started to run the conveyor chain. The speed of the conveyor, and consequently the feed rate and the extraction time, was predetermined by using the correct combination of chains and sprockets. Then the solvent pump was turned on and the con-

trol valve regulated until the rotameter reading showed the desired solvent flow. The feed of soybean flakes followed. The feed was added to the extractor at two places as shown in Figure 1, because experience in some test runs showed that it would be easier to fill the conveyor chain with flakes if feed was introduced at two places instead of one. Approximately two hours were allowed to bring the operation to steady state, which could be checked by measuring the extraction temperature and the miscella concentration at the extractor outlet. The feed rate of the flakes was measured by recording the time required to empty the containing vessel, which held about six pounds of flakes. The moisture content of the flakes was determined and the feed rate was converted to moisture-free basis. After steady state conditions of operation had been reached, a sample of the miscella was collected in a gallon-jug for future analysis. The amount of the sample taken depended on the miscella concentration so that, after removing the solvent, enough oil could be obtained. One to two gallons were usually enough for our purposes. The miscella, other than the sample taken, was collected in a 52-gallon drum and when it was full, it was fed to the pilot plant solvent recovery unit to recover the hexane. The time when the meal first came out of the drier was also recorded. The sample of meal was taken two hours later and was used to determine the residual extractables. The total time of each run varied with

the speed of the conveyor chain, or extraction time, but usually took about four hours. After the extraction run was finished, it would take two more hours to empty the unit and to clean the miscella screen, making it ready for the next run.

A total of more than twenty preliminary runs were made to find the relation of operating variables with the residual extractables in the meal. As was mentioned before, the oil was separated from the solvent by evaporating and steam stripping the miscella in the pilot plant solvent recovery unit, which gave dark colored oil. The oil samples thus obtained were not satisfactory for analysis and the results are not reported here.

Later on solvent removal was done on a bench scale with laboratory glasswares. The final traces of the solvent were removed by heating the oil in a vacuum oven. Light colored oil was obtained. Operating data of pilot plant runs No. S-1 through No. S-6 are given in Table 9.

However, it was found later that soybean flakes tended to deteriorate on storing and that the oil extracted from such flakes had higher free fatty acid contents. Thus soybean flakes were prepared freshly for each run and the pilot plant data for such runs, No. 1 through No. 10, are compiled in Table 10.

Table 9. Pilot plant data for runs No. S-1 through S-6

Run number	Rate of feed lb/hr	Rate of solvent lb/hr	Solvent-feed ratio lb/lb	Speed of conveyor chain in/min	Time of extraction min.	Average extraction temperature °F	Moisture content of flakes %	Date flaked	Date extracted
S-1	5.3	8.00	1.51	3.2	32.8	155.4	11.6	June 18	June 22
S-2	4.1	5.03	1.23	2.2	47.7	149.4	11.6	June 18	July 2
S-3	4.1	5.03	1.23	2.2	47.7	153.2	11.6	June 18	July 14
S-4	4.4	8.00	1.82	2.2	47.7	149.8	11.6	June 18	July 23
S-5	7.1	3.60	0.50	5.5	19.1	152.3	12.9	July 25	Aug. 5
S-6	7.2	2.50	0.35	5.5	19.1	155.4	11.9	Aug. 26	Sept. 1

Table 10. Pilot plant data for runs No. 1 through No. 10

Run number	Rate of feed lb/hr	Rate of solvent lb/hr	Solvent-feed ratio lb/lb	Speed of conveyor chain in/min	Time of extraction min.	Average extraction temperature °F	Moisture content of flakes %	Miscella concentration % oil
1	6.97	2.50	0.36	5.5	19.1	154.8	12.92	45.2
2	7.15	3.60	0.50	5.5	19.1	154.5	10.68	42.5
3	7.20	5.03	0.70	5.5	19.1	153.2	14.20	33.5
4	7.29	8.00	1.10	5.5	19.1	149.8	13.20	27.0
5	3.50	6.40	1.83	1.6	65.6	150.6	12.81	11.9
6	3.51	8.00	2.28	1.6	65.6	149.9	12.81	10.0
7	4.07	5.03	1.23	2.2	47.7	149.8	9.47	17.5
8	4.10	8.00	1.95	2.2	47.7	133.0	9.47	14.0
9	5.26	2.50	0.48	3.2	32.8	155.4	9.29	34.0
10	5.35	5.03	0.94	3.2	32.8	140.1	9.29	28.2

Solvent removal

The miscella collected from the extractor was first filtered through a glass funnel to remove the fines. The filtered miscella was distilled on a water bath under reduced pressure, which was produced by the suction of a water ejector. After most of the solvent was removed, the contents were transferred to a beaker and dried in a vacuum oven at 90°C for three hours. After cooling, the oil was checked for its specific gravity. If the specific gravity at 25°/25°C was within the range of 0.917-0.921, which is the standard for soybean oil recommended by the American Oil Chemists' Society, it was assumed that the solvent removal had been complete. If not, the oil was put back into the vacuum oven again until the right specific gravity could be achieved. It was noticed, however, that the color of the oil became darker if it was kept in the oven too long. Usually heating at 90°C for three hours was enough.

Analytical results

The oil quality was determined by analysis and was expressed in terms of refining loss, iodine value, saponification value, unsaponifiable matter, color, and refractive index. The determination of the free fatty acid content was actually included in the procedures for refining loss, since the amount of alkali used in the test was based on the free fatty acid content of the oil. It has been mentioned before

that for pilot plant runs No. S-1 through S-6 the free fatty acid content of the oil was high because deterioration of flakes in storing. Therefore, the oil samples were only analyzed for iodine value and saponification value and the data are compiled in Table 11, for comparison. The complete analytical data for runs No. 1 through No. 10 are given in Tables 12 and 13 and plots of refining loss, iodine value, and saponification value against residual extractables are given in Figures 3, 4, and 5, respectively. As a limiting case for comparison of the iodine value and the saponification value, the oil obtained from the Soxhlet extractor was used. The residual extractables were determined from the meals of the corresponding runs.

Table 11. Analytical data for runs No. S-1 through S-6

Run number	Free fatty acid %	Iodine value	Saponification value
S-1	0.68	127.6	195.8
S-2	0.78	118.0	194.7
S-3	1.06	86.4[a]	193.0
S-4	1.67	112.2	195.3
S-5	1.15	124.8	192.3
S-6	0.73	124.2	192.6

[a]Oil sample was very viscous when analyzed. It was probably partly polymerized on storing.

Table 12. Analytical data for runs No. 1 through No. 10
(Crude soybean oil)

Run number	Residual extractables in meal %	Free fatty acid %	Refining loss %	Iodine value (Wijs)	Saponification value	Non-saponifiable matter %	Refractive index
1	4.24	0.54	5.12	127.3	192.4	0.40	1.4739
2	3.21	0.49	5.10	126.9	192.3	0.71	1.4736
3	1.52	0.54	5.45	125.7	192.2	0.44	1.4728
4	1.10	0.54	5.66	125.5	192.1	0.73	1.4729
5	0.73	0.54	7.03	125.0	191.3	0.54	1.4723
6	0.68	0.54	7.46	124.5	190.3	0.67	1.4719
7	0.94	0.59	5.92	125.1	191.5	0.56	1.4730
8	1.40	0.59	5.54	125.7	192.2	0.44	1.4730
9	2.34	0.57	5.28	126.7	192.0	0.60	1.4731
10	1.82	0.54	5.45	126.4	192.3	0.41	1.4729
Soxhlet extractor	0.00	--	--	122.7	185.6	--	--

Table 13. Analytical data for runs No. 1 through No. 10 (Refined soybean oil)

Run number	Residual extractables in meal %	Iodine value (Wijs)	Saponification value	Refractive index	Spectrophotometric color
1	4.24	129.7	193.3	1.4738	6.4
2	3.21	129.6	193.4	1.4733	6.0
3	1.52	129.6	193.6	1.4738	6.8
4	1.10	129.2	193.4	1.4735	6.1
5	0.73	129.7	193.9	1.4738	6.5
6	0.68	129.1	193.5	1.4732	7.5
7	0.94	129.7	193.0	1.4734	7.6
8	1.40	129.5	193.4	1.4736	8.1
9	2.34	130.0	193.0	1.4731	8.2
10	1.82	129.7	193.0	1.4733	7.7

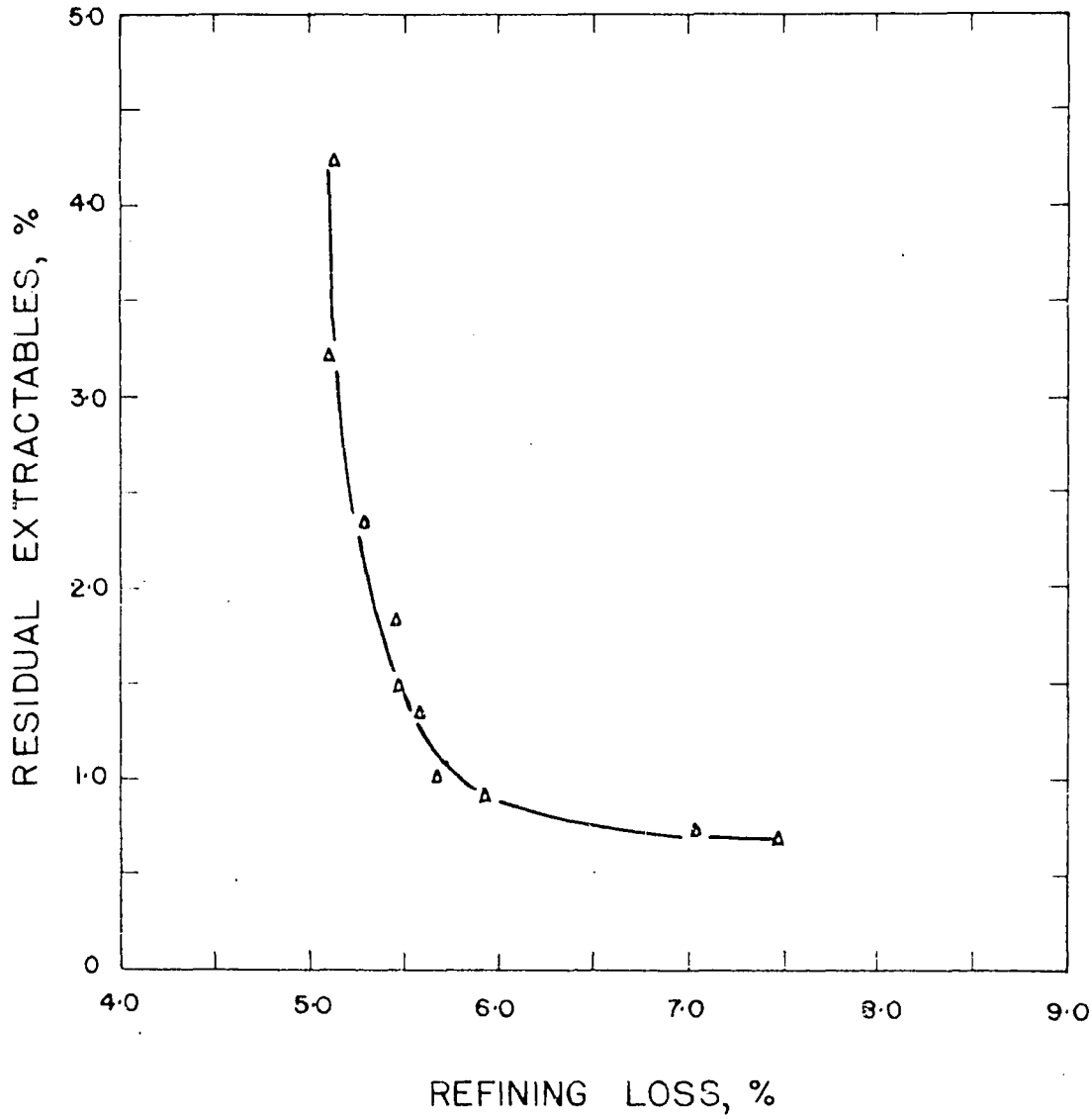

Figure 3. Correlation of refining loss and residual extractables

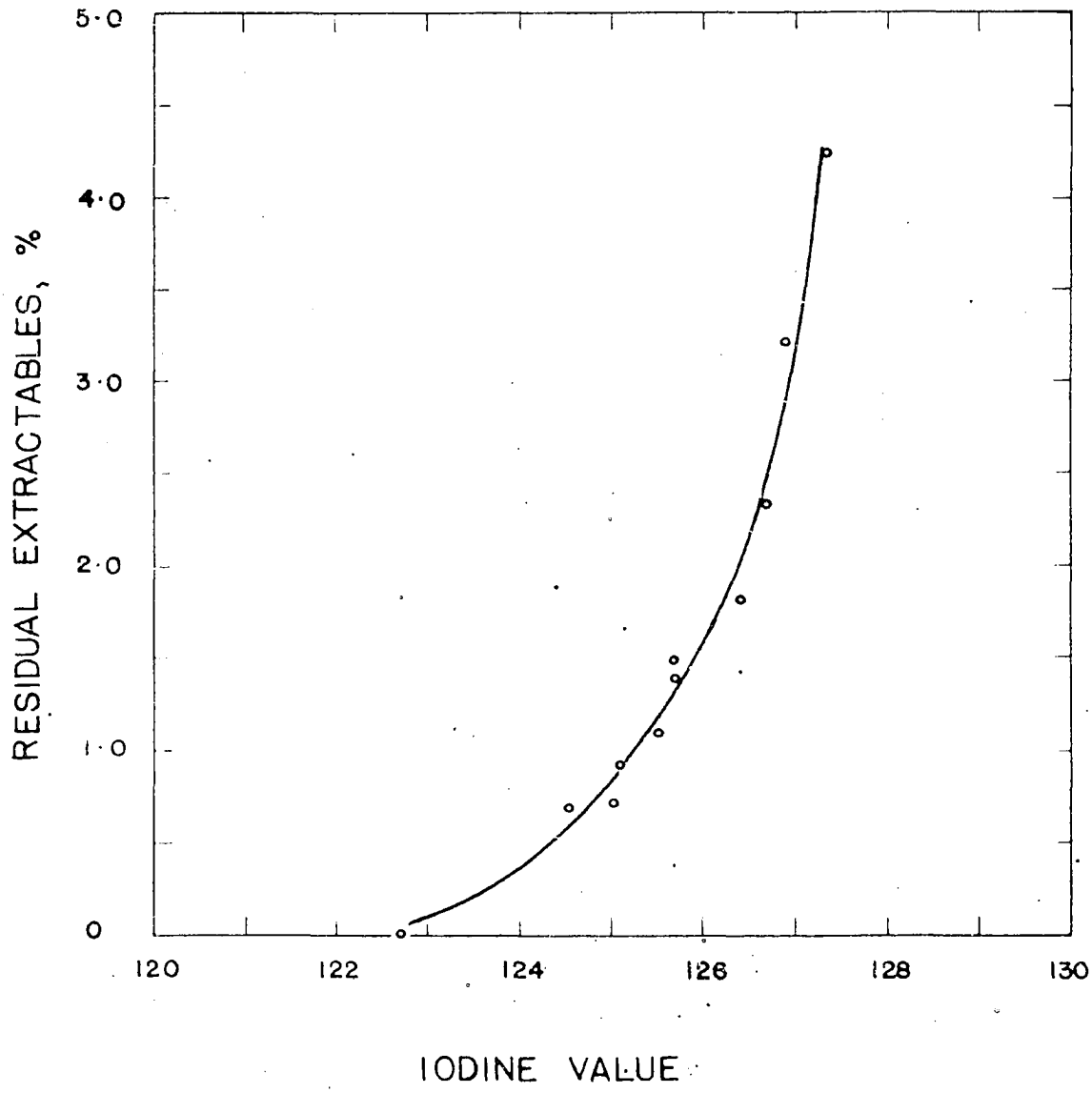

Figure 4. Correlation of iodine value and residual extractables

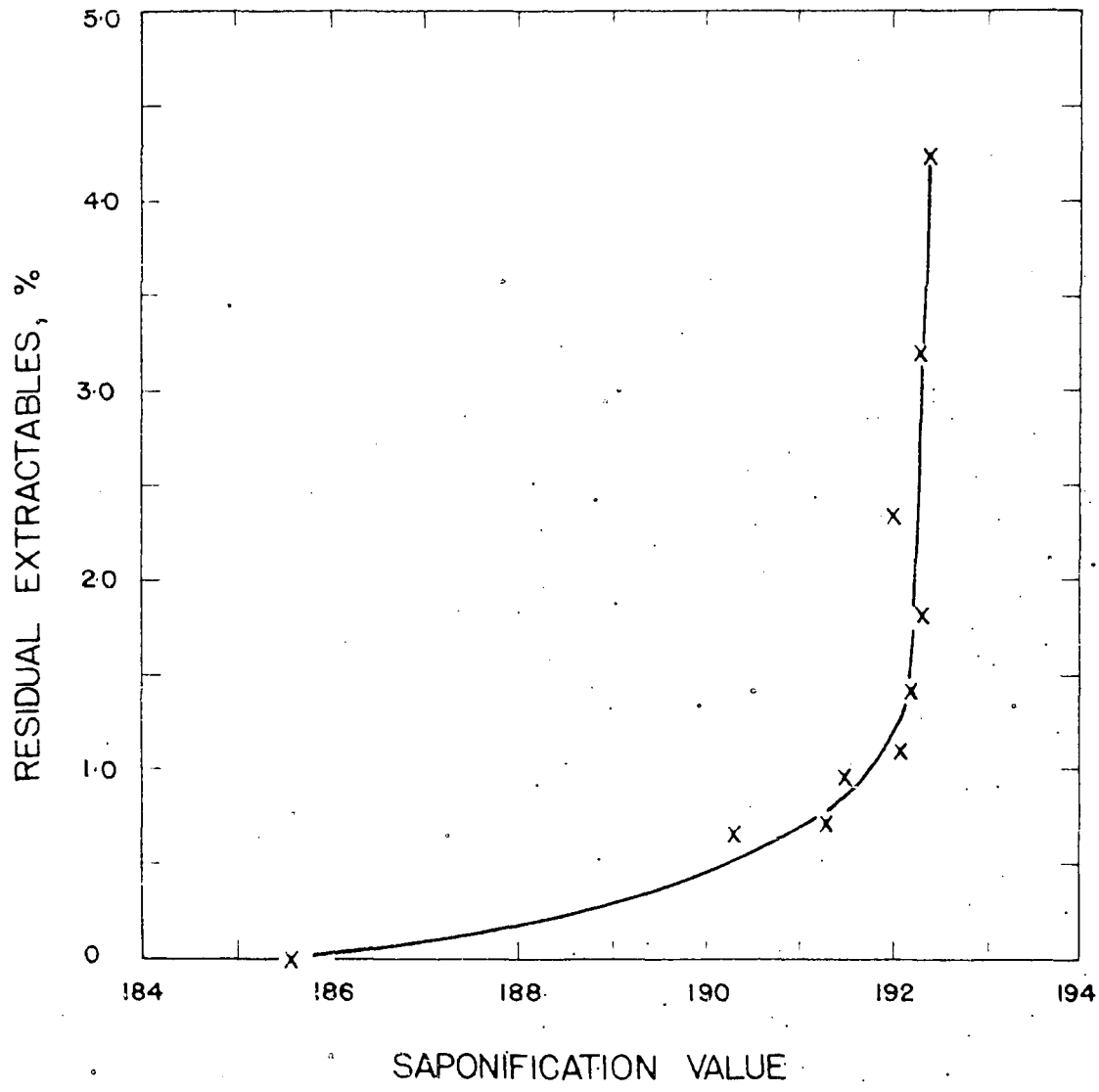

Figure 5. Correlation of saponification value and residual extractables

DISCUSSION

The continuous countercurrent extraction of soybean oil with the Iowa State University pilot plant extractor using hexane as solvent showed that the iodine value of the oil decreases with the residual extractables remaining in the meal. The results appear to be in agreement with those of Bull and Hopper (17) in multiple stage extractions, except that in continuous countercurrent extractions the oil obtained possesses an average quality of the oils from multiple stage extractions and consequently the differences in the quality are very much diluted.

The saponification value of the oil also decreases with the decrease in residual oil in the meal.

It is well-known that the oil becomes richer in phosphatides in proportion to the completeness of extraction. The phosphatides contain a range of fatty acids qualitatively identical with those present in the glycerides. However, the proportions of the different acids in the two may be quite different. An investigation of the alcohol-soluble (lecithins) and insoluble (cephalins) phosphatides had been made by Hilditch and Pedelty (32) with the following results, expressed in percentages:

Alcohol-soluble fraction: Palmitic 17.15, hexadecenoic 5.47, Oleic 18.81, linoleic 52.40, linolenic 3.62, as C_{20} unsaturated acids 1.49, and 1.03 of unsaponifiable matter.

Alcohol-insoluble fraction: Palmitic 11.47, stearic 3.67, as arachidic 1.37, hexadecenoic 8.37, oleic 5.42, linoleic (includes a little linolenic acid) 61.83, as C_{20} unsaturated acid 5.36, and 2.31 of unsaponifiable matter. As compared with the fatty acids of soybean glycerides given previously in Table 6, the proportion of saturated acids is higher in the phosphatides than in the glycerides and the ratio oleic:linoleic is markedly lower in the phosphatides than in the glycerides.

The iodine value and the saponification value are, respectively, a measure of the unsaturation and of the average molecular weight of the oil. The former is expressed in terms of the number of centigrams of iodine absorbed per gram of the sample; the latter in terms of the number of milligrams of potassium hydroxide required to saponify 1 gram of the sample. Thus, the iodine value and saponification value of the component fatty acid glycerides of soybeans can be calculated as listed in Table 14.

With the values in Table 14 it is possible to estimate quantitatively how composition of free fatty acids will effect the iodine value and the saponification value of the oil.

Scholfield and Bull (60) has been able to estimate the approximate fatty acid compositions of soybean oil in terms of the iodine value by a set of empirical equations. A rapid spectrophotometric method for determining the linoleic and

Table 14. Iodine value and saponification value of fatty acid glycerides

Common name	Systematic name	Number of C atoms	Number of double bonds	Iodine value of triglyceride	Molecular weight of triglyceride	Saponification value of triglyceride
Palmitic	Hexadecanoic	16	-	--	807.3	208.5
Stearic	Octadecanoic	18	-	--	891.5	188.8
Arachidic	Eicosanoic	20	-	--	975.6	172.5
Palmitoleic	Hexadecenoic	16	1	95.04	801.2	210.1
Oleic	Octadecenoic	18	1	86.01	885.4	190.1
Linoleic	Octadecadienoic	18	2	173.21	879.3	191.4
Linolenic	Octadecatrienoic	18	3	261.61	873.3	192.7

linolenic acid in soybean oil was described by Collins and Sedgwick (23). Paper chromatographic analysis of the glycerides has been reported by Inouye et al (33) and Kaufmann and Sohnurbusch (38). A direct determination of the saturated fatty acids was developed by Kuemmel (41). The procedure involves methanolysis of the glycerides, followed by oxidation of the unsaturated methyl esters by potassium permanganate. The undesired, acidic oxidation products are removed by alkaline washing and the saturated methyl esters thus isolated are weighed directly.

Among all the methods for direct determination of fatty acids in oils, the one worth particular mention is perhaps the gas-liquid partition chromatography originally devised by James and Martin (35) in 1952. Since then the method has been extended and improved by Ray (58), Martin and James (46), James and Martin (34), Craig and Murty (24), Orr and Callen (50), and Lipsky (43).

The separations obtained by gas-liquid chromatography are essentially parallel to those obtainable by distillation, but good separation can be achieved much more easily and it is possible to work with much smaller quantities.

There seems to be no appreciable change in the free fatty acid content of the oil with the completeness of extraction, if the soybean flakes used are freshly prepared. However, soybean flakes tend to deteriorate upon storage. The data of runs No. S-1 through S-4 showed an increasing percentage of

free fatty acid in the extracted oil with increased period of time on storage. The iodine value of the oil from old flakes is lower than that of the oil extracted from freshly prepared flakes under similar operating conditions, but the difference in saponification value is comparatively small.

The proper refining treatment removes substantial amounts of free fatty acids, phosphatides, color bodies, and other materials from the crude oil. Since the last portions of oil extracted contain progressively more phosphatides, it is conceivable that the refining loss increases rapidly with the completeness of extraction. Analyses of the quality of the refined soybean oil in different runs showed no appreciable difference in iodine value, saponification value, or refractive index.

It should be pointed out here that the cup method of determining refining loss usually gives higher value than the actual loss in the plant. In the refining plant some new methods, such as the degumming procedure described by Hayes and Wolff (30) and the method of conducting refining in two stages as recommended by Beal (11), are preferred in order to reduce refining losses to a minimum.

Refractive index is an important property of fats and oils not because of any direct interest in the refraction of light by the lipid but because the index of refraction is relatively easy to determine, and is characteristic of a given oil, and

because it can be correlated with other less easily determined properties. Majors and Milner (44) found that the refractive indices of soybean oils of any one crop year can be closely correlated with the iodine value, but that there are considerable variations from one crop year to another. Zeleny and Neustadt (71) concluded that there is a straight line relationship between the refractive index and the iodine number of soybean oils. Pickering and Cowlishaw (56), as the result of examination of hundreds of samples of fresh soybean, linseed, refined cottonseed, and peanut oils, were able to correlate the refractive index to its respective iodine value by a set of empirical equations, with correction of the influence of free fatty acid and molecular weight. The data obtained in this project, however, do not show clearly the relationship of the iodine value and the refractive index.

The characteristic yellow-red color of most fats and oils is due to the presence of various carotenoid pigments. It is convenient to think of the many pigments which occur in crude soybean oil as being of three types: those which are largely removed during refining and which may be associated with iron or phosphorus or both, those remaining in the oil after refining which are adsorbable by bleaching clays, and those which change to a colorless form or are destroyed upon heating the oil to a high temperature during deodorization.

Scholfield and Dutton (61) reported that the color of soybean lecithin is due to carotenoids. The brown color, very

likely an aldehyde amine reaction product, is largely formed by heating of the oil during the solvent-stripping operation. It is not increased by drying the gums under vacuum for three hours at 80°C but it is increased on heating at 100°C under the same conditions.

At early stages of this project, solvent-stripping was carried out in the pilot plant recovery unit, which gave an oil of dark color. Later on, solvent removal was done on a bench scale with laboratory glasswares and the final traces of solvent were removed by heating the oil in a vacuum oven for three hours at 90°C and 28 inches vacuum. This seemed to be a good approach, referring to the above mentioned data of Scholfield and Dutton (61). Perry and co-workers (55) studied the vapor pressure of soybean oil, and reported the pressure to be 0.001 mm at 254°C and 0.050 mm at 308°C. Therefore, the vapor pressure at 90°C is negligible and there is no appreciable loss of oil during the heating operation.

The carotenoids are readily adsorbed by Fuller's earth or activated carbon, hence the color of an oil pigmented solely by these compounds may be reduced to any desired value by sufficient intensive treatment with adsorbents.

The carotenoid pigments are also to some degree unstable to heat, hence oils are bleached by high-temperature treatment, as in steam deodorization.

It was supposed that as a means of process control the

miscella concentration could be evaluated by spectrophotometric determination of the color of the miscella, just as density-composition relations had been used for process control. Investigations showed that below 25 percent of oil in the miscella, the Beer's law relation held. However, one drawback of this method is that the color of the crude soybean oil is a quality which usually varies in greater range than the density of the oil, and consequently the spectrophotometric method for determining the miscella concentration is less accurate than the density-composition method.

No definite relation was established between nonsaponifiable matter and completeness of extraction. As Andre and Maille (5) have pointed out the A.O.C.S. method for determining unsaponifiable matter by extracting with petroleum ether is not reproducible. The authors claimed that extraction of unsaponifiable substances with ethyl ether could give the most satisfactory results.

Similar studies of continuous countercurrent extraction of soybean oil were done by Choudhury[a] in glassware rate extraction apparatus. The results showed that there was a continuous increase of phospholipids with the decrease of residual extractables. The trend is the same as for the pilot plant refining loss in this project. However, Choudhury's[a] experi-

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[a]Choudhury, R. Basu Roy, Ames, Iowa. Data on solvent-extracted soybean oil. Private communication. 1960.

ments gave iodine values varying from 125.4 to 127.5, which increased with the decrease of residual extractables. The trends seem to be opposite to those of the pilot plant data in this project and to those of Bull and Hopper (17) with multiple stage extractions, though the actual differences in the iodine value are small. Perhaps it can be explained as there are no significant variations in iodine value with completeness of extraction.

CONCLUSIONS

Experiments of continuous countercurrent extraction of soybean oil in the Iowa State University pilot plant extractor, using commercial hexane as solvent, have led to the following conclusions:

1. The iodine value of crude oil decreases as the residual extractables in the meal decrease. Samples analyzed for iodine value varied from 124.5 to 127.3 with corresponding residual oil from 0.68 to 4.24 percent.

2. The saponification value of crude soybean oil decreases with the residual extractables in the meal. Samples analyzed for saponification value varied from 190.3 to 192.4 as the residual oil varied from 0.68 to 4.24 percent.

3. Refining loss increases with completeness of extraction. Above 1.0 percent residual oil the difference in refining loss is small but below 1.0 percent residual oil the refining loss increases rather rapidly. The refining loss is found to be 5.55 and 7.46 percent with 1.10 and 0.68 percent residual oil, respectively.

4. There seems to be no particular relation between nonsaponifiable matter and completeness of extraction.

5. There is no appreciable difference in iodine value, saponification value, and refractive index of the refined oils from different runs.

6. The color of refined oil varied from 6.0 to 8.2 but the variation is believed to be due more to the process of solvent-stripping than to the completeness of extraction.

7. The overall variation of soybean oil quality with completeness of extraction is small with continuous counter-current extractions. The oils obtained from different runs all have characteristics within the range specified by the American Oil Chemists' Society, as given in Table 7.

8. Owing to the higher refining losses incurred, there will be no actual gain in refined oil if the extraction is carried on to below 1.0 percent residual oil content.

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